

FORMATION OF NITROGEN OXIDES IN AERATED METHANE FLAMES

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INTRODUCTION

An investigation to determine the kinetics of the formation of the oxides of nitrogen produced in aerated methane flames is currently in progress at IGT. Under controlled flow conditions, the location and concentration of the oxides of nitrogen — nitric oxide, NO, and nitrogen dioxide, NO₂ — were experimentally measured in a premixed bunsen-type flame and on a premixed flat flame. The compositions of the primary stream (fuel-oxidant) and the secondary stream were varied. This paper summarizes the highlights of the work to date. The study is sponsored by the American Gas Association under its PAR (Promotion-Advertising-Research) Plan.

EXPERIMENTAL TECHNIQUE

The data on NO₂ were obtained with a Mast nitrogen dioxide analyzer. The concentrations of NO were initially determined by use of a catalytic probe which converted the NO to NO₂ for later analysis with the Mast. The NO concentrations are currently being obtained by homogeneously oxidizing the NO to NO₂ with oxygen at high pressure prior to analysis. Spot checks by the phenyldisulfonic acid technique are made on the concentration of oxides of nitrogen in the water condensed from the flue gas sample stream. These have not shown significant quantities of nitrogen oxides in most cases.

The reproducibility of the data is very good for runs made on the same day. The worst variations observed for runs on different days were about ± 2 ppm. Most of the data showed smaller variations than this.

EXPERIMENTAL RESULTS

Figure 1 shows a bunsen flame which had a primary feed stream consisting of methane with 67 percent of the stoichiometric air required for complete combustion, and a secondary feed stream of air. Figure 2 shows the concentrations of NO and NO₂ measured at various positions in this flame. It can be seen that NO forms in a narrow region near the outside edge of the flame. It then diffuses both toward the center of the burner and into the secondary air stream. It oxidizes rapidly to NO₂ in the secondary air stream. Very little NO₂ is found in the burning gas.

Table 1 shows the average concentration of NO + NO₂ (NO_x) at each height above the burner. This average value corresponds to the concentration of NO_x which would have to be uniformly distributed over the cylindrical cross-section to yield the same total concentration shown at each height in Figure 2. Table 1 shows that the formation of NO_x occurs only where the flame is present. Above the tip of the flame, i.e., at heights greater than 7.2 cm, the concentration is seen to remain constant within experimental uncertainty. This suggests that the flame is acting as more than a source of heat, and may be participating chemically in the formation of NO_x.

Table 1.—AVERAGE NO_x CONCENTRATION AT VARIOUS HEIGHTS ABOVE
FLAMEHOLDER WITH A CONICAL FLAME OF 67+ PRIMARY AERATION
(Primary Flow Rate 15.6 CF/hr)

Height Above Flameholder, cm	Average NO_x Concentration, ppm	
	Corrected for Temperature Profile	Uncorrected
0.5	--	1.3
1.8	--	1.7
3.7	3.6	2.9
7.2	4.8	4.5
9.7	--	3.9
15	4.5	4.2

Figure 3 shows the results obtained when argon was substituted for nitrogen in the primary stream, with air retained as the secondary stream. The concentration of argon was varied so that the difference between the heat capacities of argon and nitrogen would not be a factor. The data show a lower concentration of NO_x when argon is substituted for nitrogen. Thus, it is seen that the nitrogen which^x reacts to form NO_x is supplied by both the primary and secondary streams, with somewhat more being^x supplied by the secondary.

Tables 2 and 3 show the effect of primary mixture flow rate (heat input) and of primary aeration on NO_x concentration at a height of 15 cm above the burner. The

Table 2.—EFFECT OF PRIMARY MIXTURE FLOW RATE (67% PRIMARY AIR)
ON THE CONCENTRATION OF NO_x 15 cm ABOVE FLAMEHOLDER

Primary Mixture Flow Rate, CF/hr	NO_x at Various Radial Positions, ppm		
	0.0 cm	1.2 cm	2.4 cm
12.1	2.7	4.1	3.7
15.6*	3.1 ± 1.0	4.5 ± 0.9	3.5 ± 0.5
20.0	3.5	4.2	3.6
25.0†	1.2 ± 0.5	5.7 ± 0.3	4.8 ± 0.1

* Average of 4 runs

† Average of 2 runs

Table 3.—EFFECT OF PRIMARY AERATION ON THE CONCENTRATION OF NO_x
15 cm Above Flameholder

Primary Aeration,	Primary Mixture Flow Rate, CF/hr	NO_x at Various Radial Positions, ppm		
		0.0 cm	1.2 cm	2.4 cm
67.3*	15.6	3.1 ± 1.0	4.5 ± 0.9	3.5 ± 0.5
67.3	20.0	3.5	4.2	3.6
50.0	18.2	1.9	4.4	3.4
67.3†	25.0	1.2 ± 0.5	5.7 ± 0.3	4.8 ± 0.1
90.0†	30.0	4.8 ± 1.1	5.1 ± 0.5	5.4 ± 0.4
110.0†	29.1	3.1 ± 0.1	2.8 ± 0.2	3.0 ± 0.2
120.0	26.3	1.2	1.7	1.9

* Average of 4 runs

† Average of 2 runs

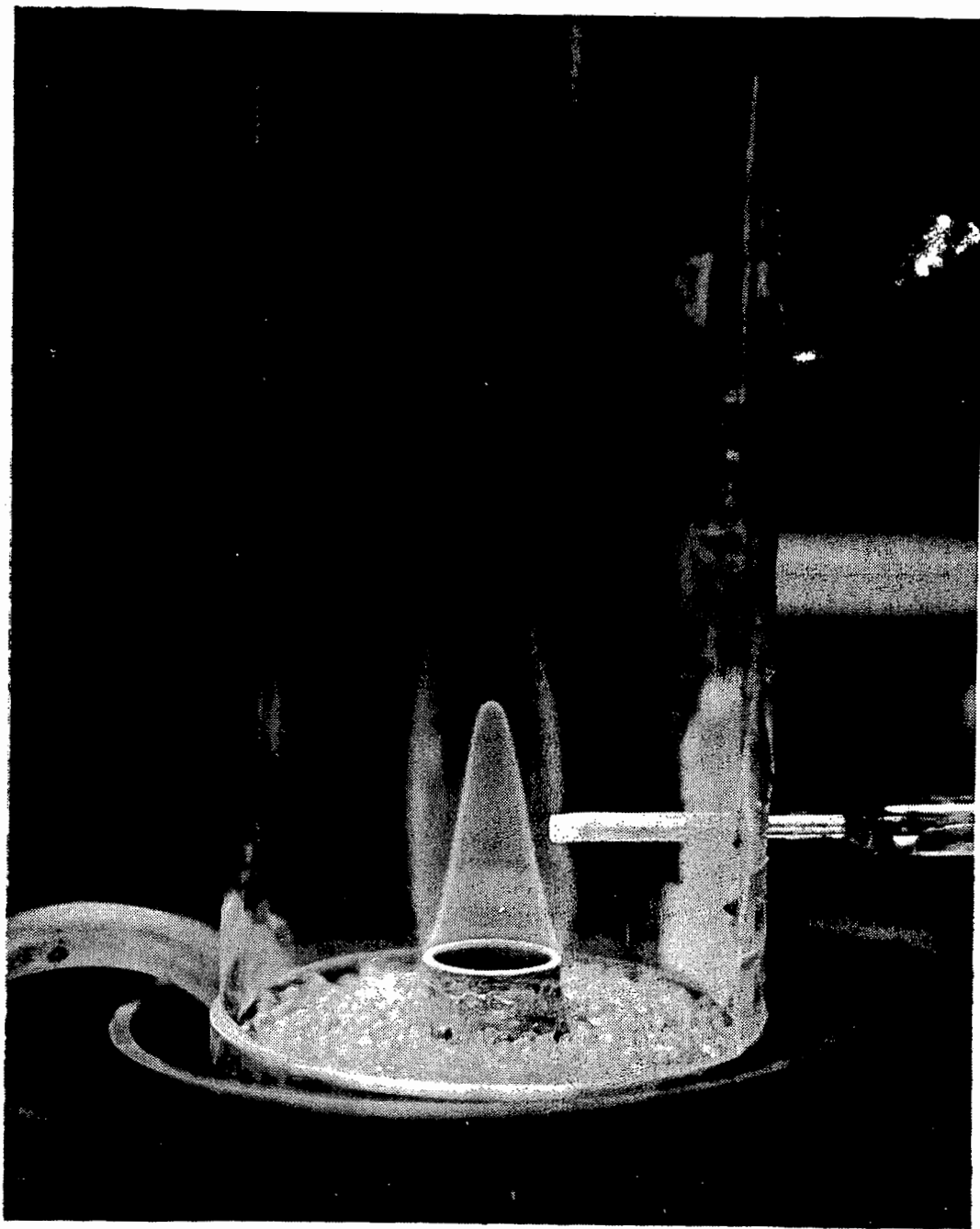


Figure 1.—QUARTZ PROBE AND 67% AERATED FLAME

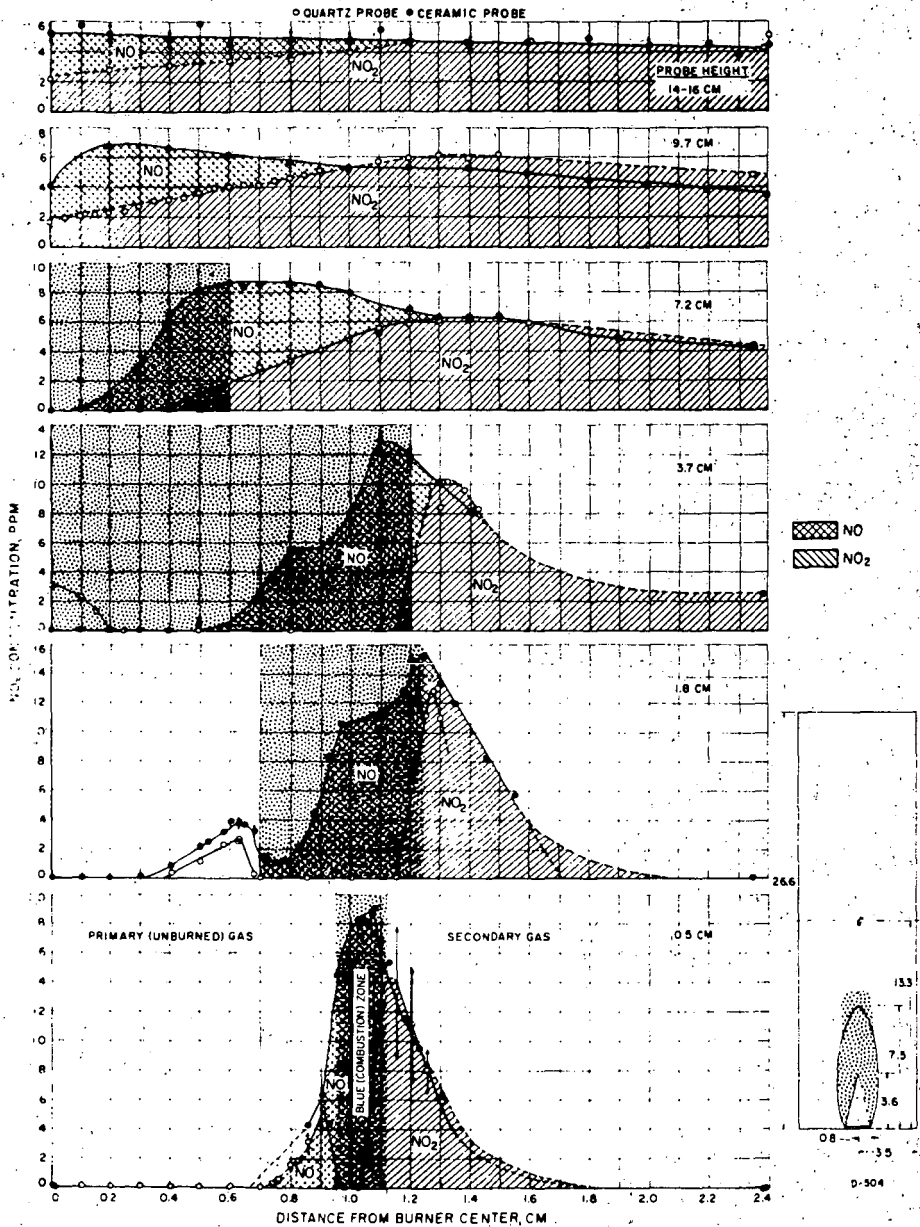


Figure 2.—NITROGEN OXIDE PROFILES AT VARIOUS HEIGHTS WITH 67% PRIMARY AERATED CONICAL FLAME

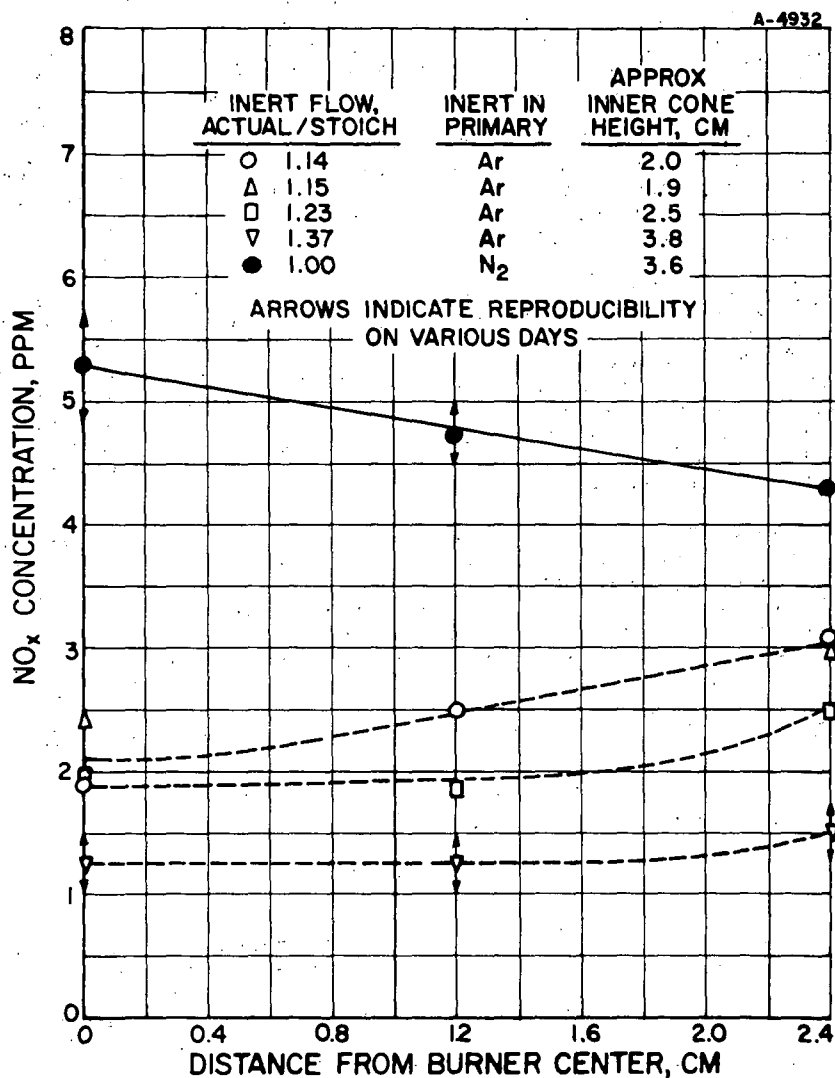


Figure 3.—CONCENTRATION OF NO_x 15 CENTIMETERS ABOVE THE FLAMEHOLDER OF A CONICAL CH₄-Ar-O₂ FLAME WITH 67% OF STOICHIOMETRIC O₂ IN THE PRIMARY STREAM

primary mixture flow rate has no apparent effect over the range of 12 to 20 CF/hr. There appears to be a small change in the concentration of NO_x as the input is increased to 25 CF/hr. The flow rate of the secondary stream has no effect over the same range.

The effect of primary aeration is not large over the range of 67 to 90 percent primary air. However, a strong decrease in the concentration of NO_x is observed when the primary mixture is made fuel-lean. Figure 4 shows the NO_x and NO_2 concentration profiles of a flame with 110 percent primary aeration. In contrast to the fuel-rich primary mixture (Figure 2), the primary oxide of nitrogen that is present is NO_2 , rather than NO . The flame with the fuel-lean primary has only a single, small combustion zone as opposed to the two larger combustion zones with the fuel-rich primary. This may account for the decreased NO_x with the fuel-lean primary.

The shape and position of the reaction zone for the formation of NO_x from a bunsen or conical flame made a kinetic analysis difficult. Consequently, the experimental work was changed from a bunsen to a flat flame stabilized by a flameholder consisting of a collection of stainless steel capillary tubes. A more detailed series of data are being obtained with this burner.

One of the most interesting observations illustrated is in Figure 5, where the concentration of NO_2 along the centerline is shown as a function of height above the burner. The NO_2 is seen to form very close to the flame (which is at a height of about 0.1 cm), and then rapidly decompose. The NO_2 concentration decreases to zero with the fuel-rich and stoichiometric primary mixtures. However, some NO_2 is found at all heights above the burner with the fuel-lean primary mixtures. These data were obtained with nitrogen as the secondary gas. A similar effect is observed when argon is the secondary. However, the decomposition of NO_2 is greatly decreased when air is the secondary.

Figure 6 shows the effect of this decomposition on the relative concentrations of NO and NO_2 when an argon or air secondary is used with a primary mixture of 100.5 percent aeration. It is seen that there is more NO_2 present at a height of 1.1 cm with air than with argon. However, in either case, the primary oxide of nitrogen is NO near the burner centerline, but it is NO_2 near the secondary. Figure 7 shows that almost no NO is present at 0.1 cm above the burner. NO_2 is the primary oxide of nitrogen at all radial positions.

There are three significant observations to be drawn from this stoichiometric flame:

- 1) NO_2 is the oxide of nitrogen which is formed in the flame.
- 2) Some of this NO_2 decomposes to NO .
- 3) NO also forms by another mechanism in the combustion products above the flame.

These observations do not necessarily contradict the data from the bunsen flame, since there are a considerable number of differences between the two systems.

There are two regions of formation of NO_x by a flat flame. Figure 8 shows that NO_2 is formed from a methane-air primary stream with an argon secondary. This NO_2 , which must have formed in the flame, is seen to decompose. Figure 9 shows that NO_2 is formed from a methane-argon-oxygen primary stream with an air secondary. This NO_2 , which forms where the primary and secondary stream are mixing, does not appear to decompose to any significant extent. Temperature differences between these two regions may explain the different decompositions observed, since the same relative effect is noted when NO_2 is added to the primary mixture of a methane-argon-oxygen flame with an argon secondary. The decomposition is much greater near the center of the burner than near the secondary. We

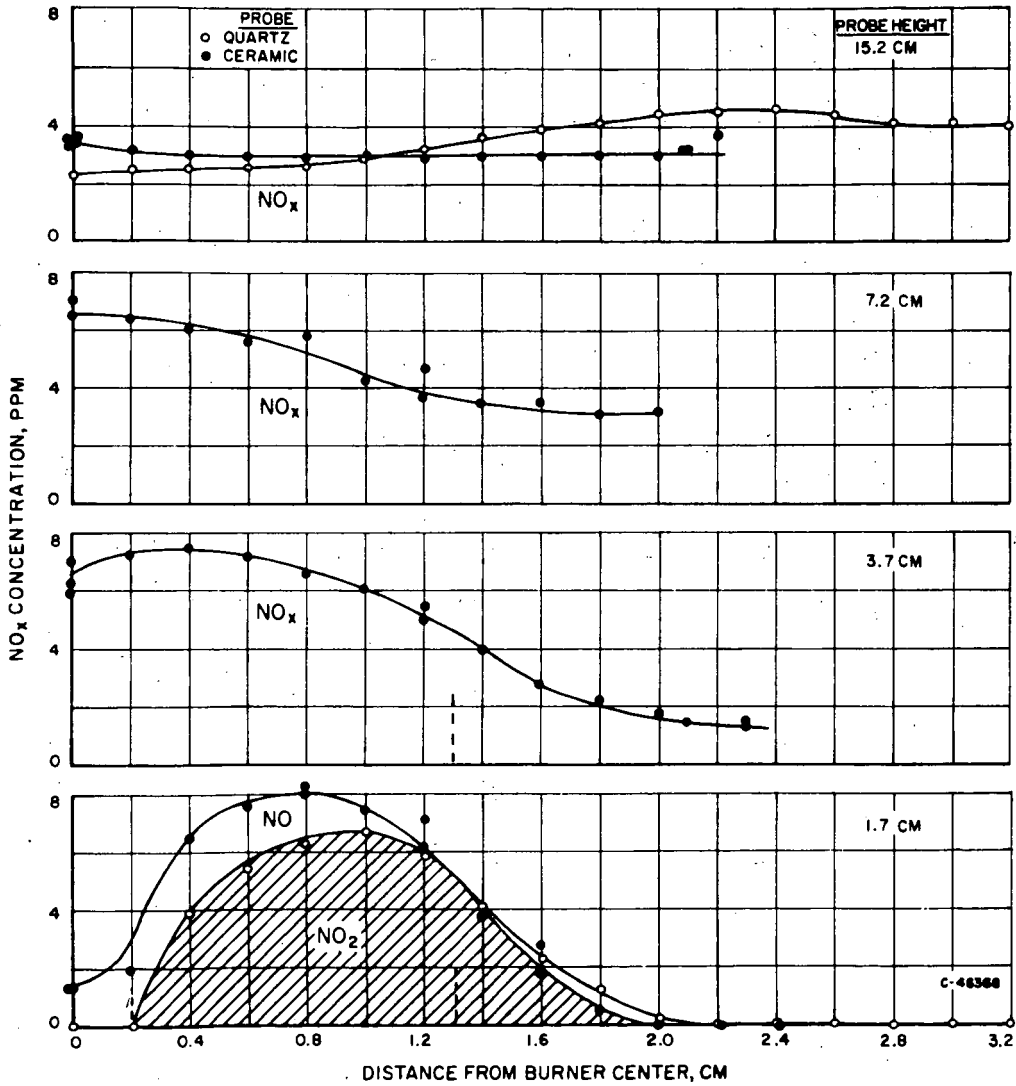


Figure 4.— NO_x CONCENTRATION PROFILES AT VARIOUS HEIGHTS WITH A 110% PRIMARY AERATED CONICAL FLAME

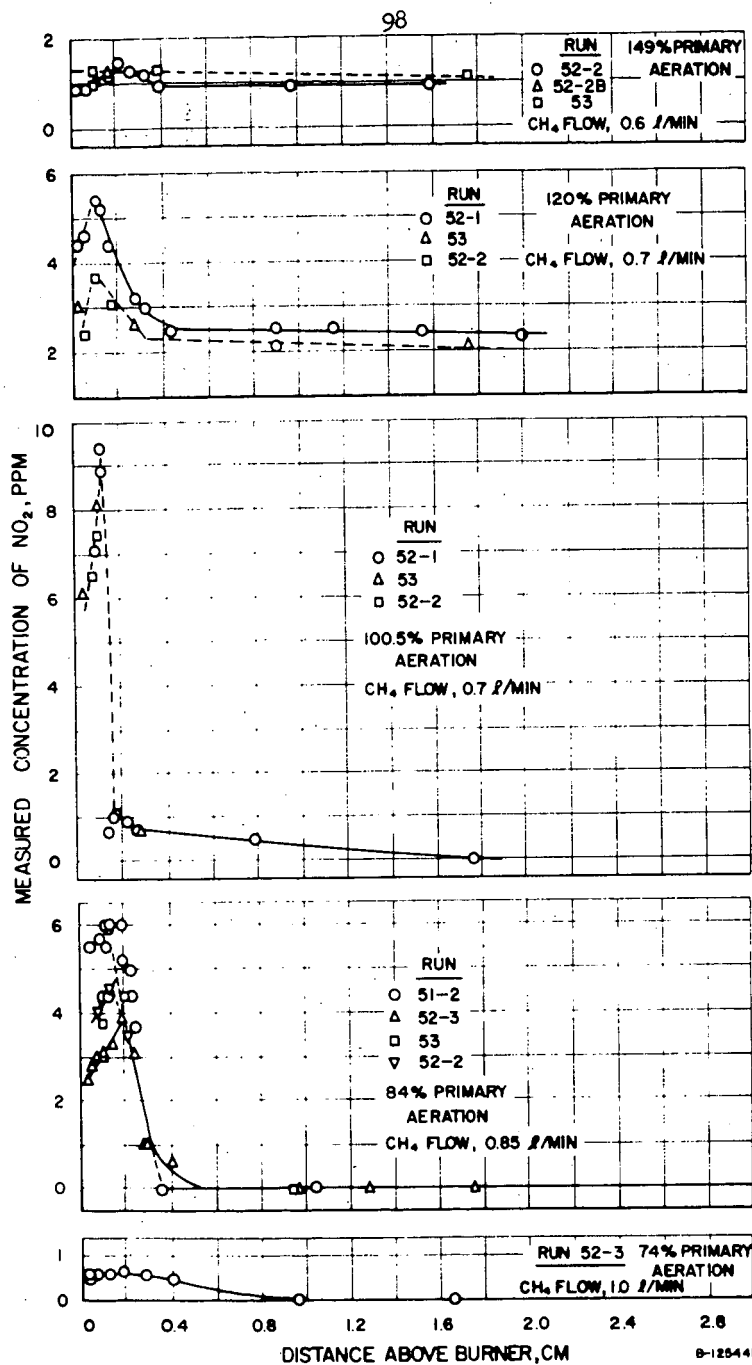


Figure 5.—AXIAL CENTERLINE CONCENTRATION PROFILES OF NO_2 FROM FLAT METHANE-AIR FLAMES WITH A SECONDARY NITROGEN ATMOSPHERE

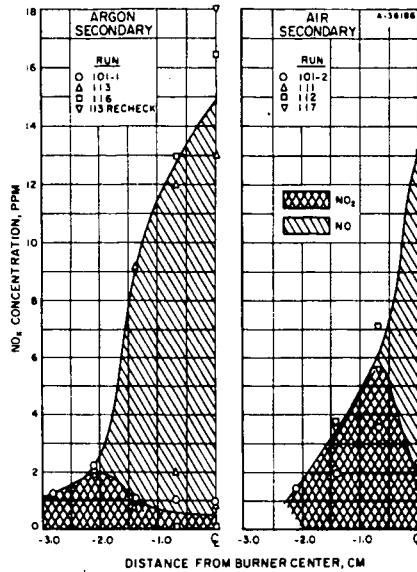


Figure 6.—NO_x CONCENTRATION FOR A CH₄-AIR STOICHIOMETRIC FLAME AT A HEIGHT OF 1.1 cm ABOVE THE BURNER

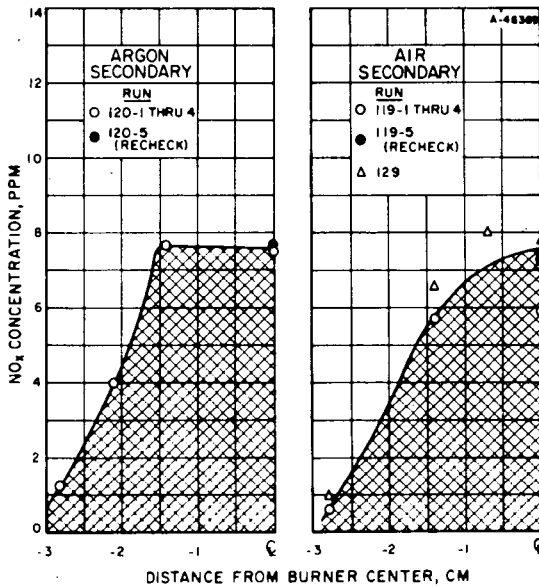


Figure 7.—NO_x CONCENTRATION FOR A CH₄-AIR STOICHIOMETRIC FLAME AT 0.1 cm ABOVE THE BURNER

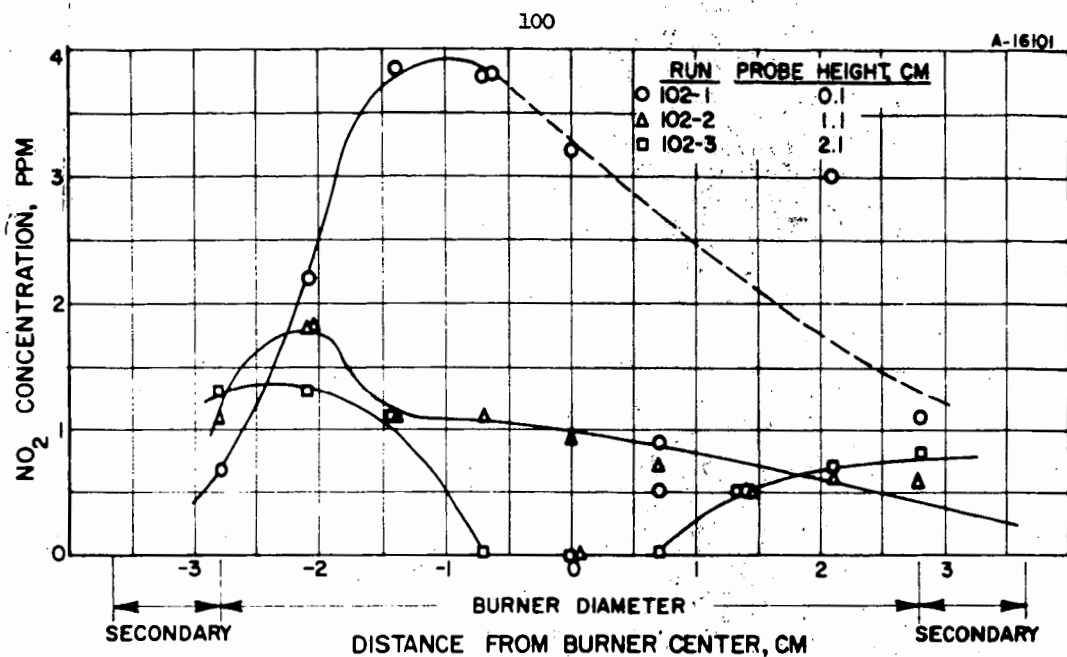


Figure 8.—FORMATION OF NO₂ FROM A STOICHIOMETRIC FLAT CH₄-AIR FLAME WITH A SECONDARY ARGON STREAM

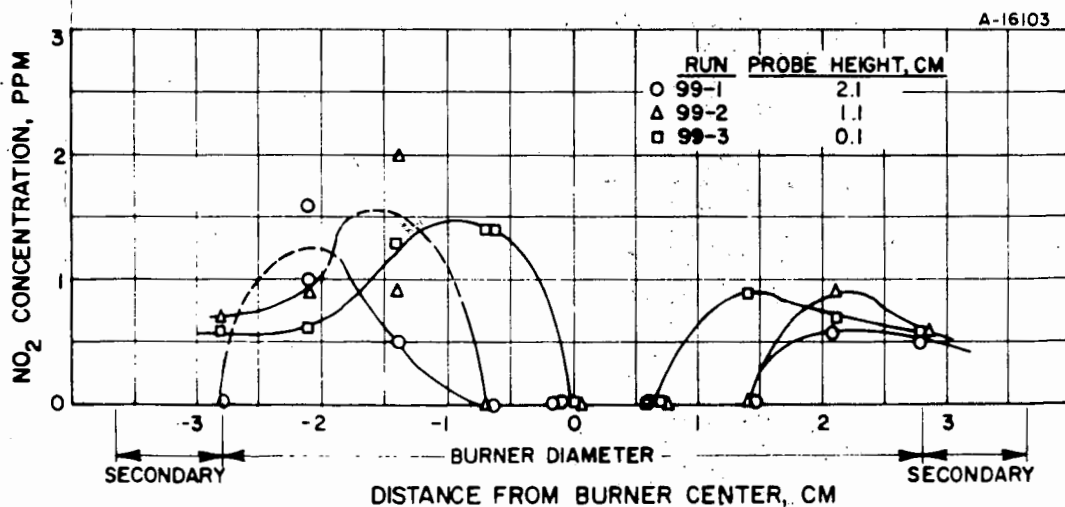


Figure 9.—FORMATION OF NO₂ FROM A STOICHIOMETRIC CH₄-Ar-O₂ FLAME WITH A SECONDARY AIR STREAM

are aware that there is some oxidation of NO to NO₂ in our sampling system. At present, the fraction oxidized appears to be small. We are interpreting the measured NO₂ as being primarily from the flame.

Theoretical equilibrium and kinetic studies are currently in process. Figure 10 shows the calculated concentration of NO_x in equilibrium¹ with the combustion products from flames of various compositions and various temperatures. At these temperatures, (above 1500°K), the ratio of the concentration of NO to that of NO₂ is more than 300:1. This ratio increases as the temperature increases or the oxygen concentration decreases.

The region where NO_x forms in the bunsen flame has relatively steep axial and radial temperature gradients. The estimated temperature range is from 2200° to 3100°R. The flat flame provides a radial region of more than 2.4 cm of very uniform temperature. The axial temperature gradient is only about 25°C/cm. The temperature above the flat flame has been estimated, with corrected thermocouple readings and published correlations,²⁻⁴ to be about 1500° ± 100°C (2700°R).

Thus, there are no indications that total concentrations in excess of equilibrium are being formed from stoichiometric or fuel-lean flames. However, the ratio of NO to NO₂ is not characteristic of the high-temperature equilibrium. This may be due to the oxidation in the sampling system.

The kinetics of this system are extremely complex because of the flame reactions. However, it is possible to compare the values measured in this system with the amount of NO that would be formed in air heated to the same temperature for the same length of time. The kinetic model (in which M represents any other species) used for this calculation is:

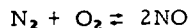
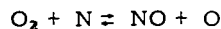
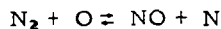
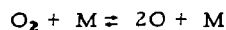
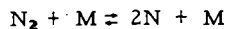


Table 4 gives the calculated rates at various temperatures. It is of interest to note that the rates of the bimolecular reaction and the atomic reactions to form NO are comparable at these temperatures. At higher temperatures, the atomic reactions will predominate.

Table 4.—RATES OF FORMATION OF NITRIC OXIDE IN AIR
AT VARIOUS TEMPERATURES

Temperature, °K	Rate of Formation of Nitric Oxide, ppm/sec	
	NO = 100 ppm	NO = 10 ppm
1600	0.90	1.02
1800	69	73
2000	2150	2210

The time required for the combustion products to pass from 0.1 to 1.1 cm above the burner is about 0.026 second. During this time, the stoichiometric combustion products are observed to form a 10 ppm increase in NO_x.

If the same time factor is applied to the kinetics of heated air, the calculated concentrations are 1.8 ppm at 1800°K, and 57 ppm at 2000°K. It should be noted that:

- 1) The rate constants for this kinetic model are not well established, and the values

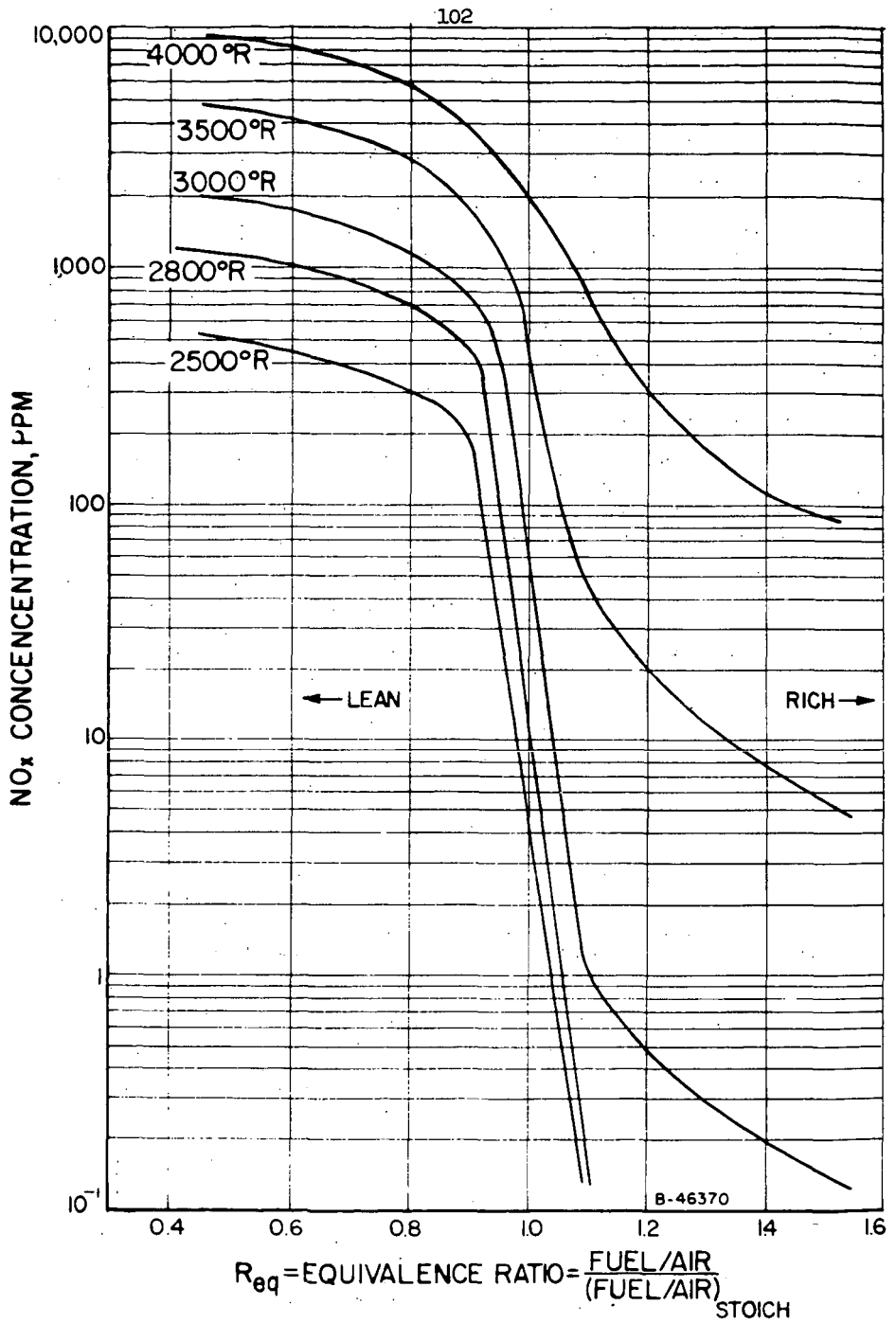


Figure 10.—EQUILIBRIUM OF NO_x WITH COMBUSTION PRODUCTS OF VARIOUS METHANE-AIR FLAMES

used in this calculation are among the highest that were found.⁵

2) The oxygen concentration of air is much larger than that of the stoichiometric combustion products by about 2 orders of magnitude.

3) The estimated temperature of the system is close to 1800 °K.

Thus, it appears likely that, upon completion of the theoretical analysis and with accurate temperature and composition measurements, it will be found that nitrogen oxides form in a flame faster than in heated air.

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